

Comprehensive Chiral Amino Acid Method for Future Enceladus Astrobiology Missions

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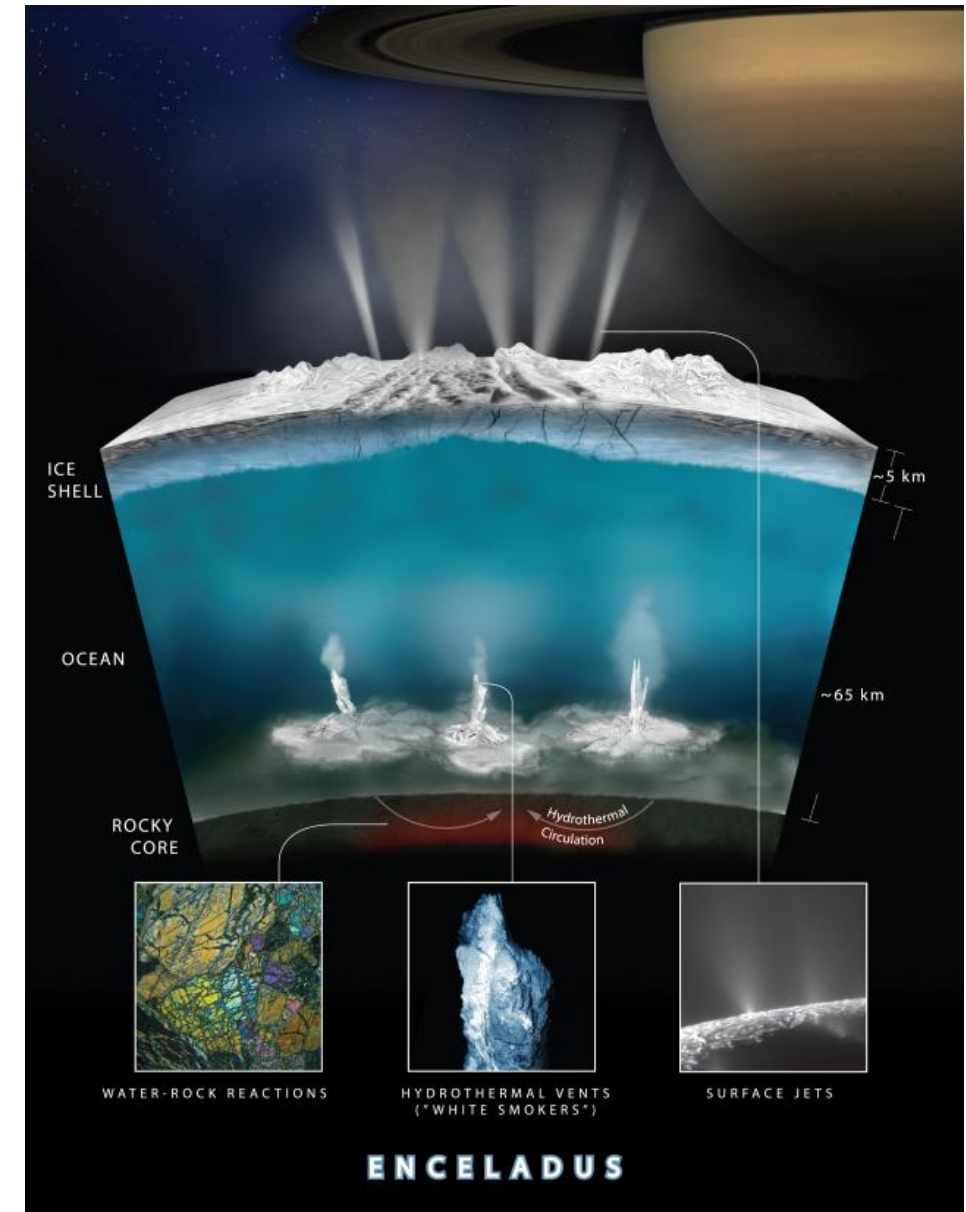
Amino acids and Enceladus?

Cassini revealed

- Water ice and water vapor
- Simple organic molecules in the gas phase and heavy organics in dust
- Tiny grains of silica
- Unexpectedly large amounts of hydrogen gas.

Active ocean-rock interface

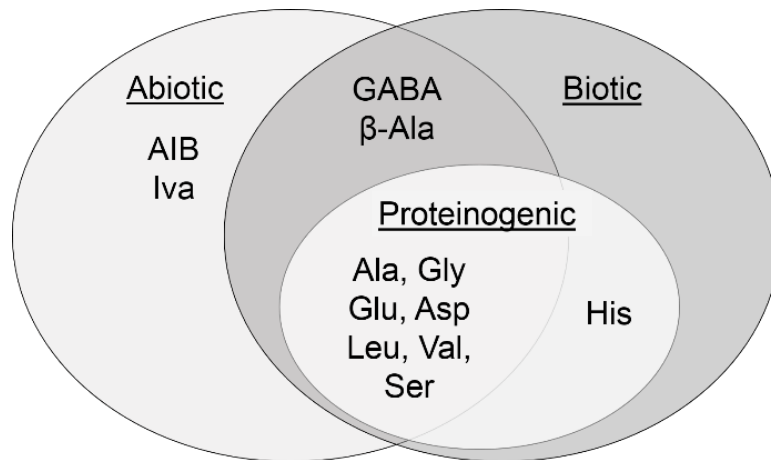
- Generating amino acids?
- Origin of life or prebiotic chemistry?



NASA/JPL-Caltech/Southwest Research Institute

Amino acid biosignatures

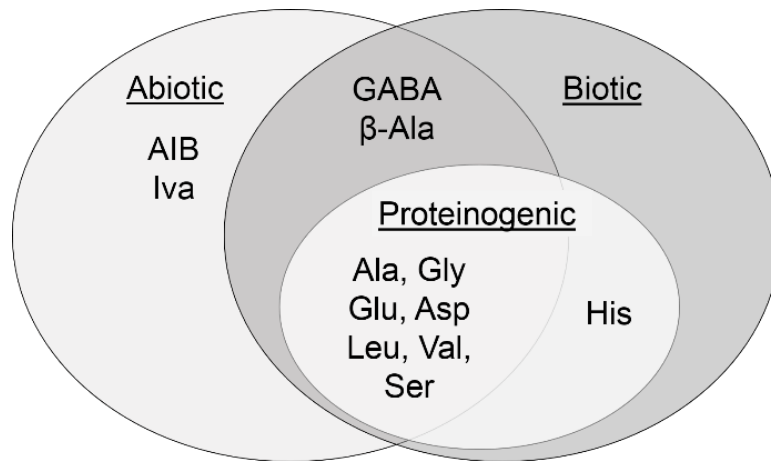
1. Type



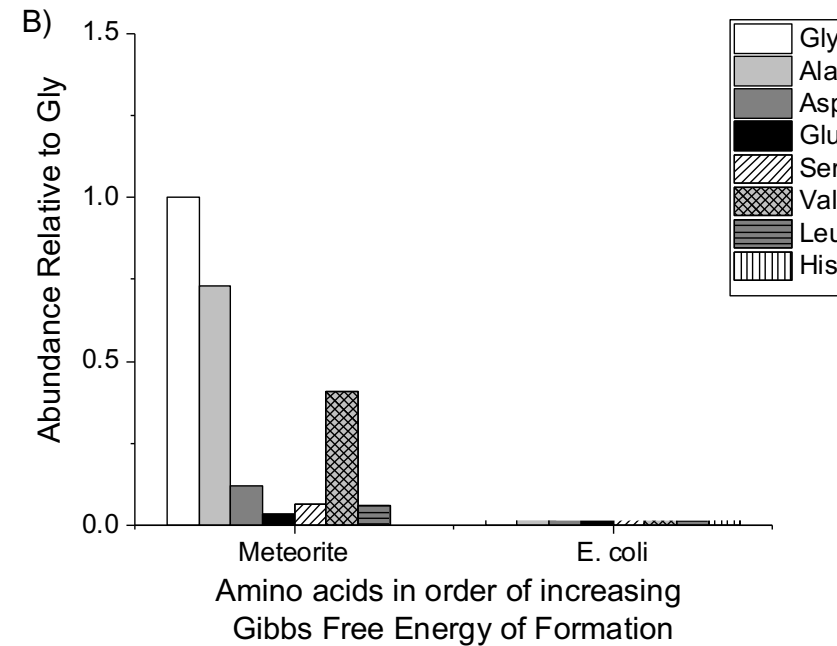
Most abundant amino acids found in biotic and abiotic samples

Amino acid biosignatures

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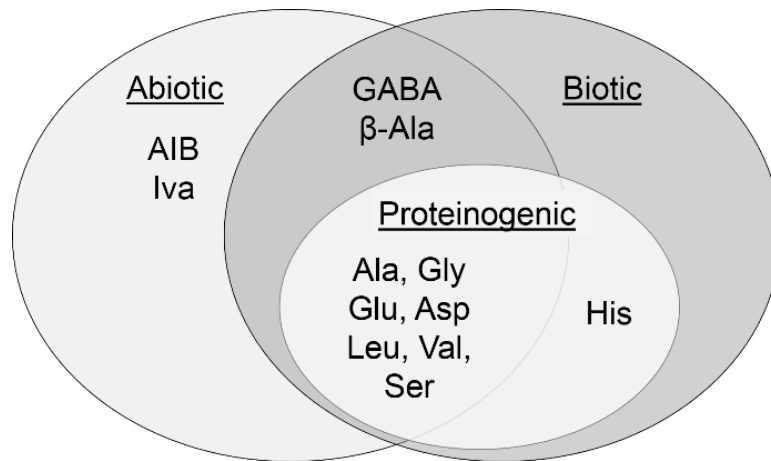
2. Relative abundance to Gly



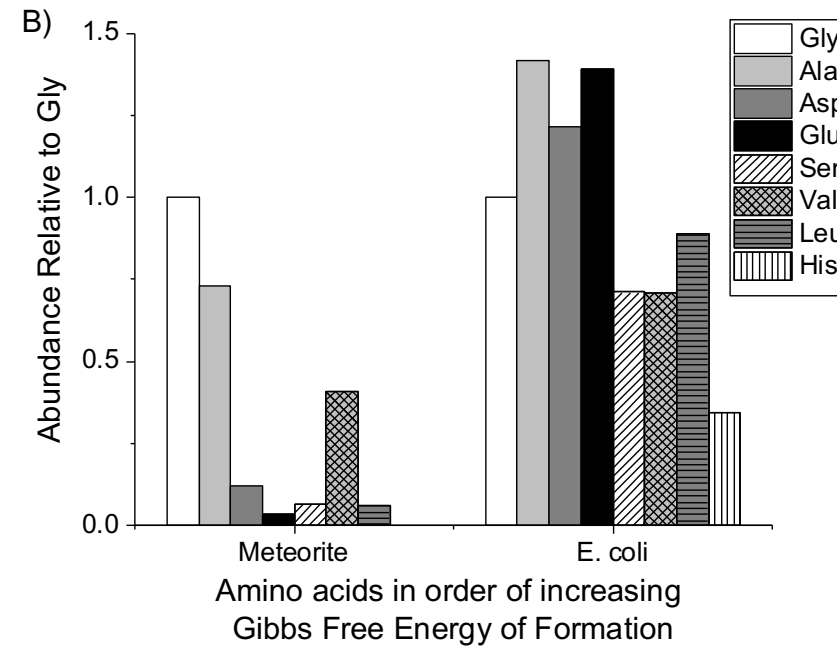
Most abundant amino acids found in biotic and abiotic samples

Amino acid biosignatures

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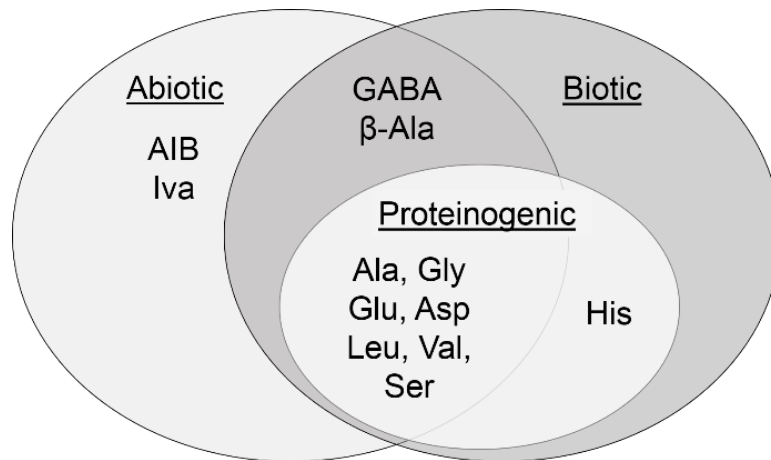
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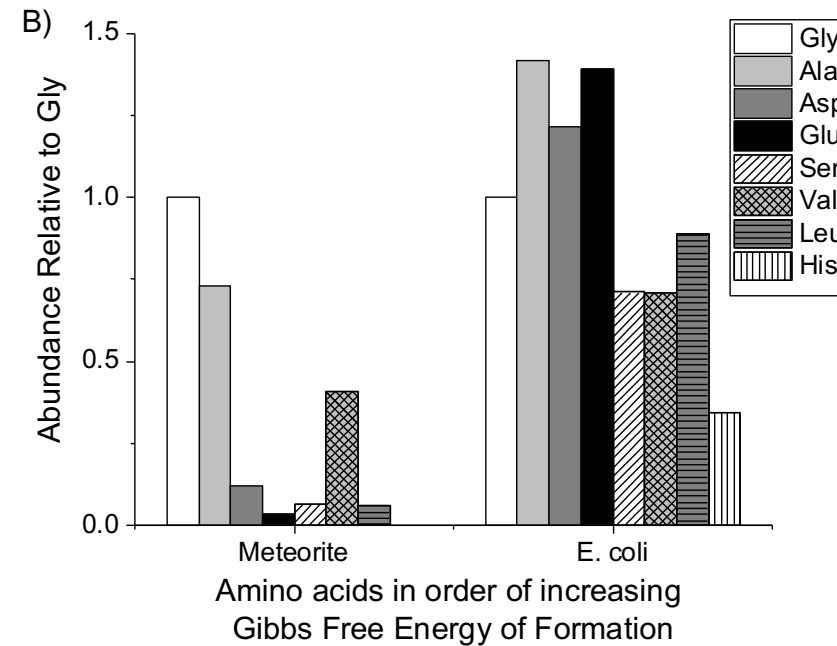
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Amino acid biosignatures

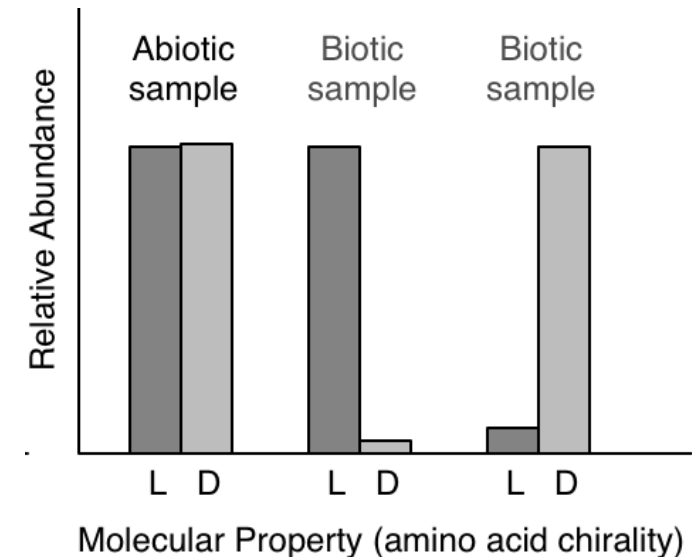
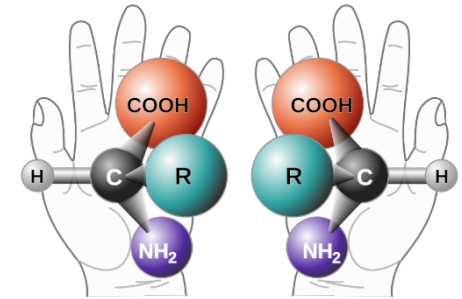
1. Type



2. Relative abundance to Gly



3. Chirality



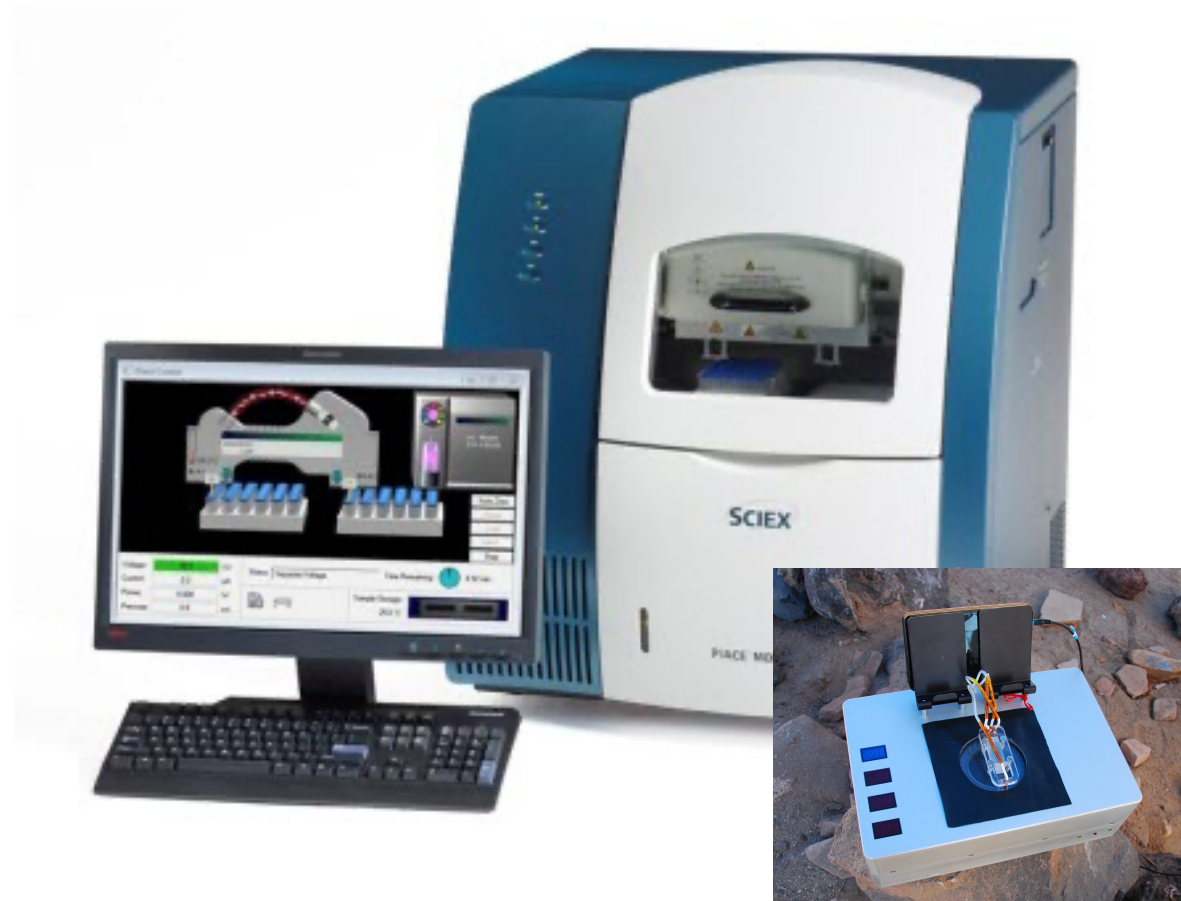
Most abundant amino acids found in biotic and abiotic samples

Voltage driven separations: Capillary and microchip electrophoresis

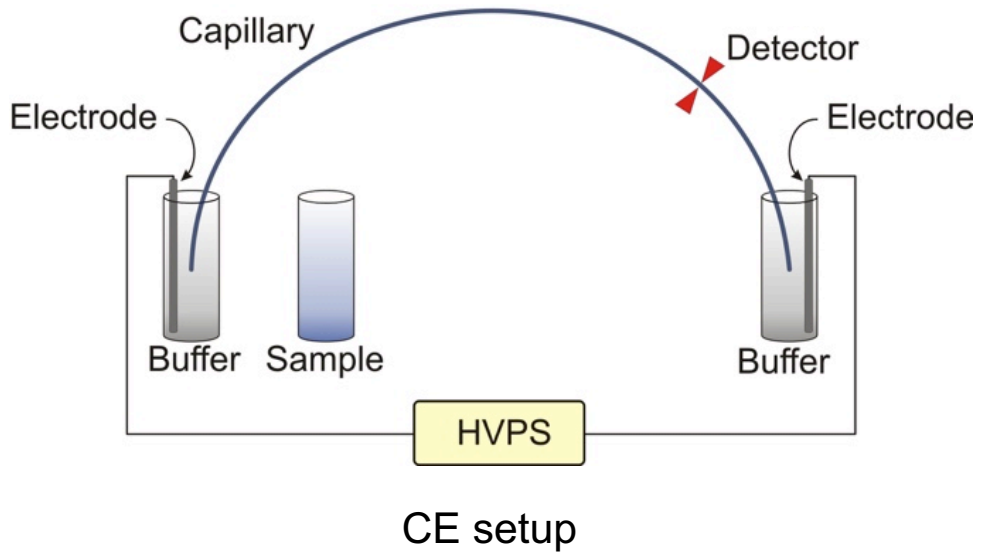
Separation is needed to individually address many species in a mixture with chiral resolution

Benefits of Electrophoresis:

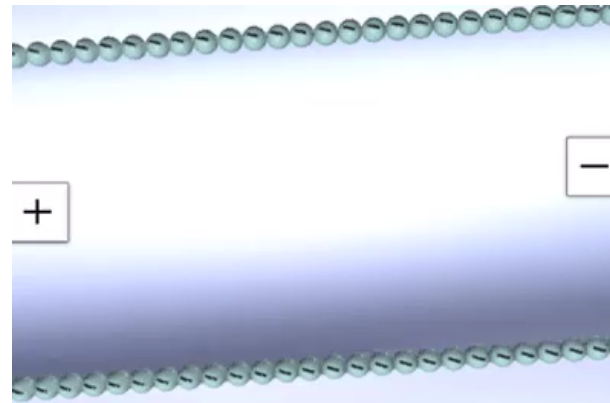
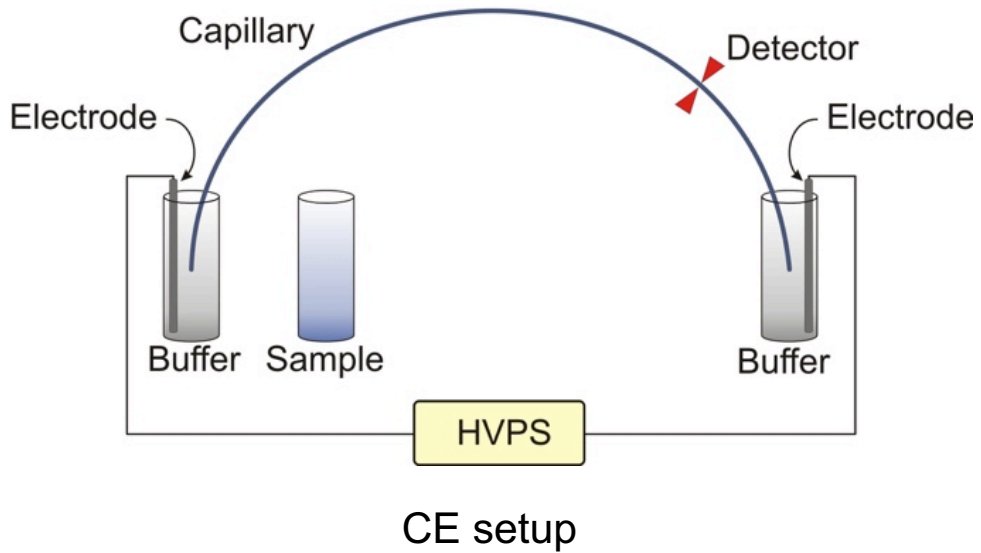
- High efficiency separations
- Low limits of detection (ppt) when coupled to LIF
- Used on a wide variety of samples
- Miniaturizable platform



Voltage driven separations: Capillary and microchip electrophoresis

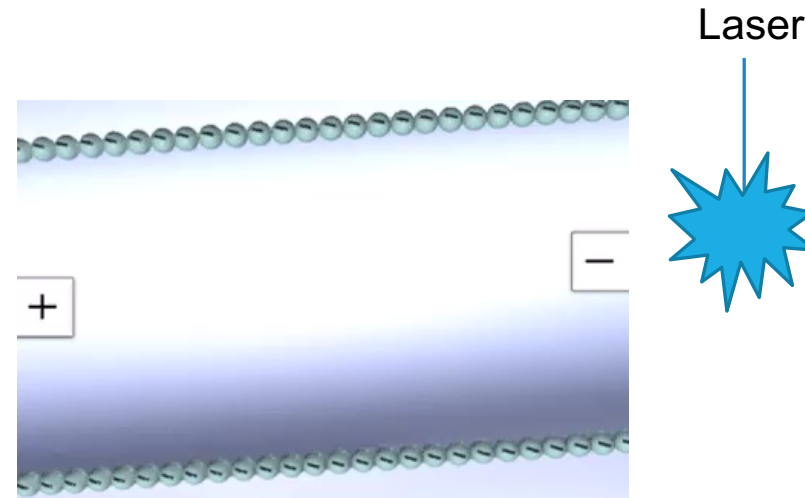
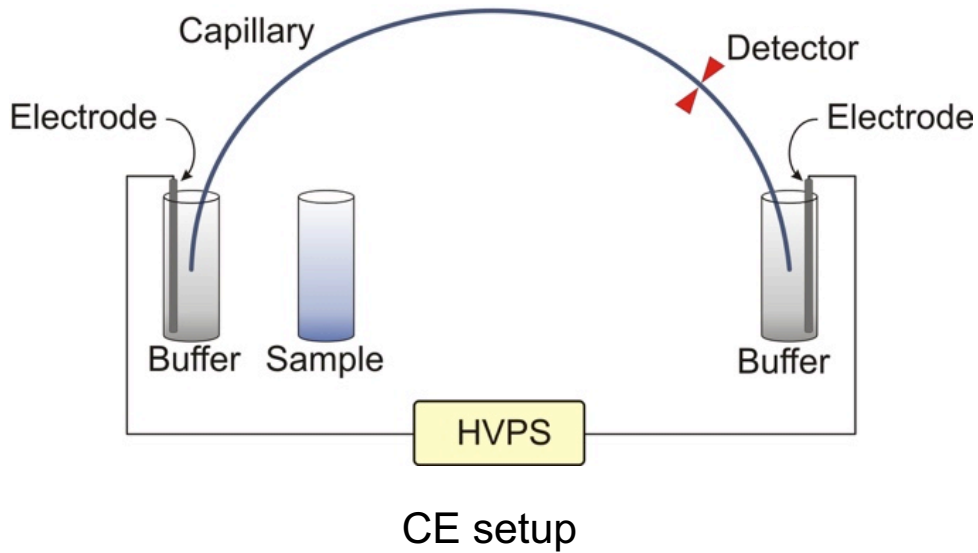


Voltage driven separations: Capillary and microchip electrophoresis

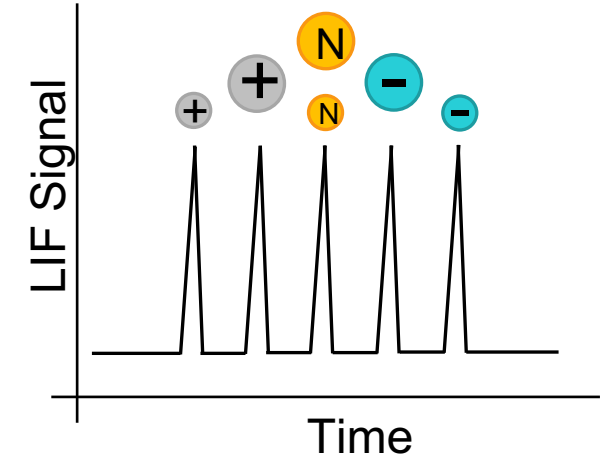


Separation based on
size:charge

Voltage driven separations: Capillary and microchip electrophoresis



Separation based on
size:charge



Electrophoretogram for
identification and quantification

Most capable published method for detection of chiral amino acids

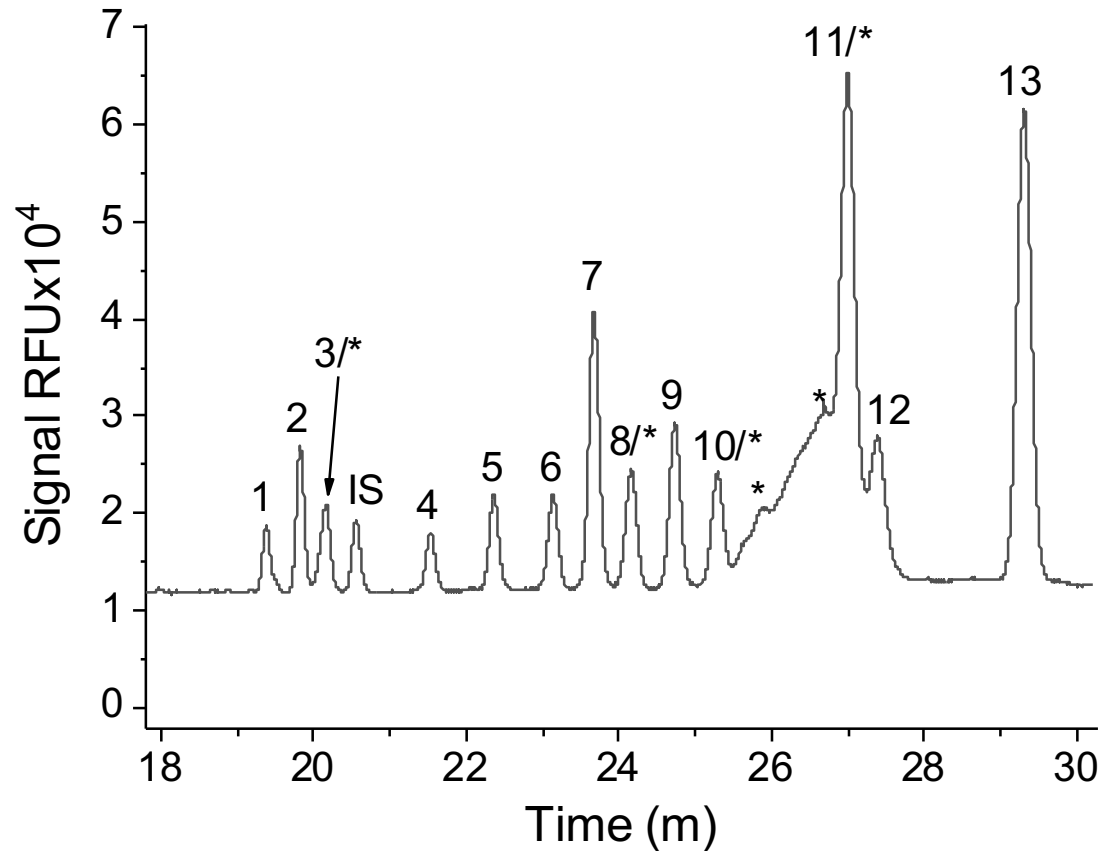
analytical
chemistry

Article

pubs.acs.org/ac

Enhanced Resolution of Chiral Amino Acids with Capillary Electrophoresis for Biosignature Detection in Extraterrestrial Samples

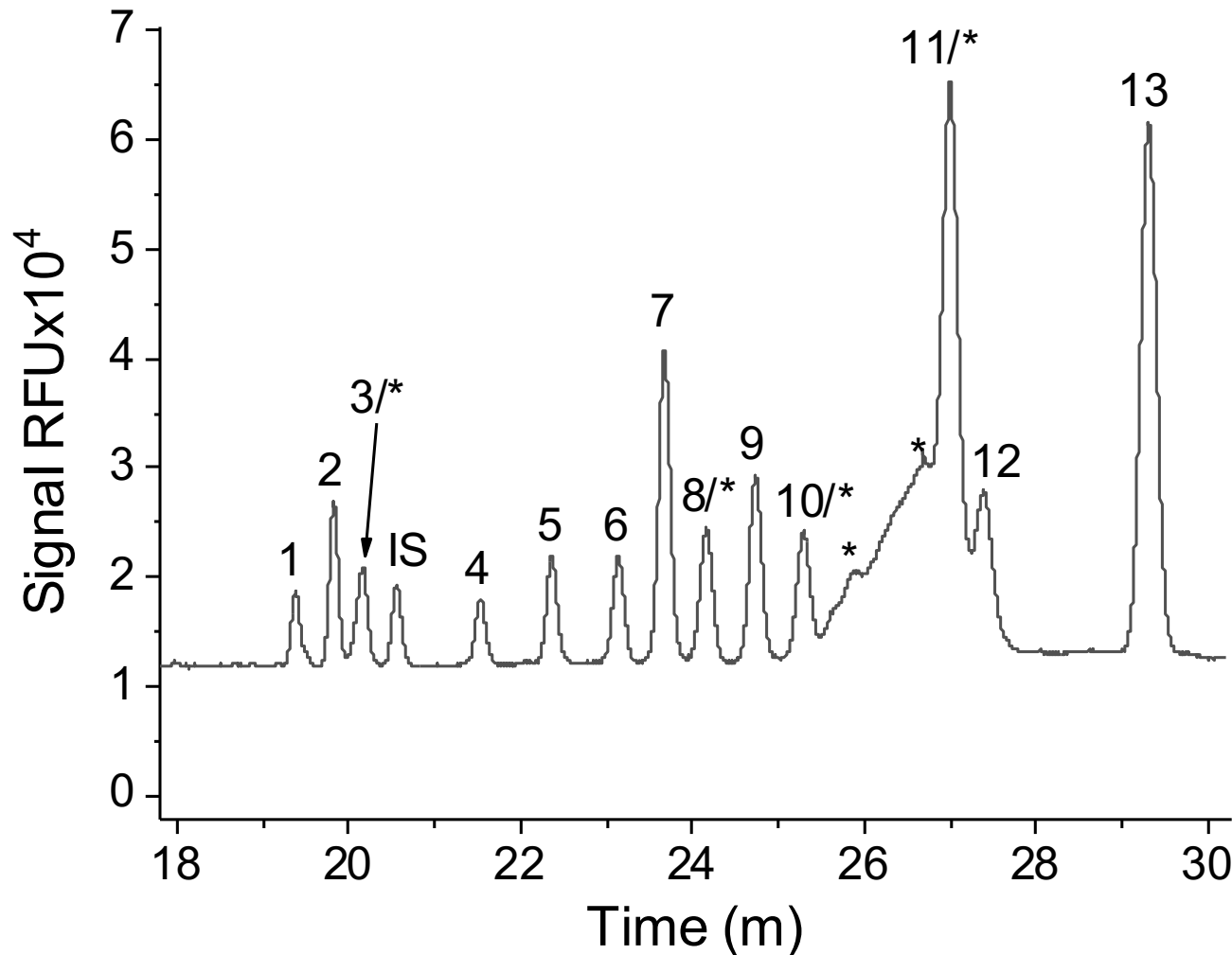
Jessica S. Creamer,[✉] Maria F. Mora, and Peter A. Willis*



Peaks:

1. D-His
 2. D-Leu
 3. D-Val
 - IS. L- β -HomoLeu
 4. L-His
 5. L-Leu
 6. D-Ser
 7. GABA;
 8. L-Val
 9. D-Ala
 10. L-Ser
 11. β -Ala
 12. L-Ala
 13. Gly
- *Dye side products

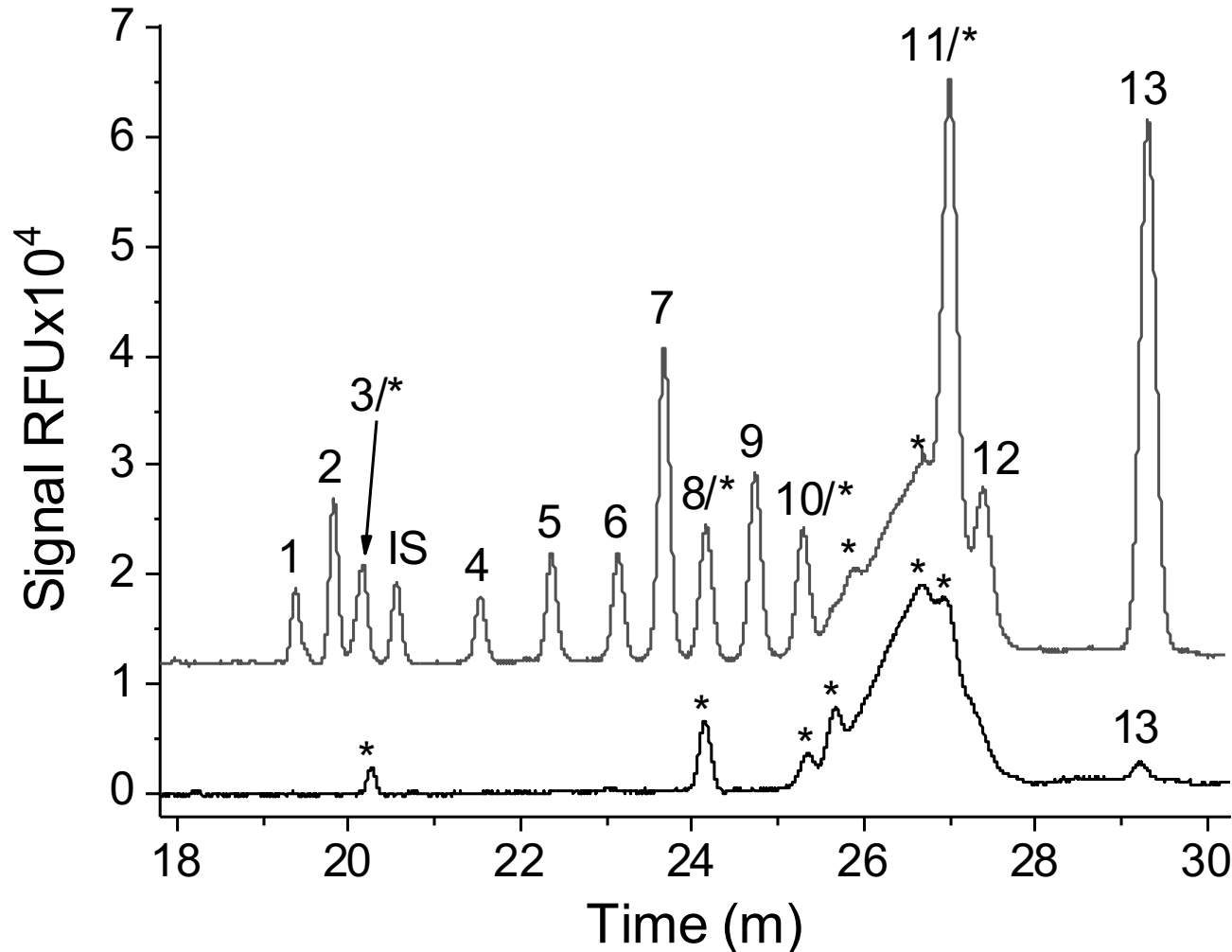
Most capable published method for detection of chiral amino acids



Updated LODs

Peak Number	Amino acid	LOD (nM)
1	D-His	3
2	D-Leu	1
3	D-Val	1
4	L-His	1
5	L-Leu	1
6	D-Ser	1
7	GABA	1
8	L-Val	1
9	D-Ala	10
10	L-Ser	10
11	β-Ala	25
12	L-Ala	25
13	Gly	3

Most capable published method for detection of chiral amino acids

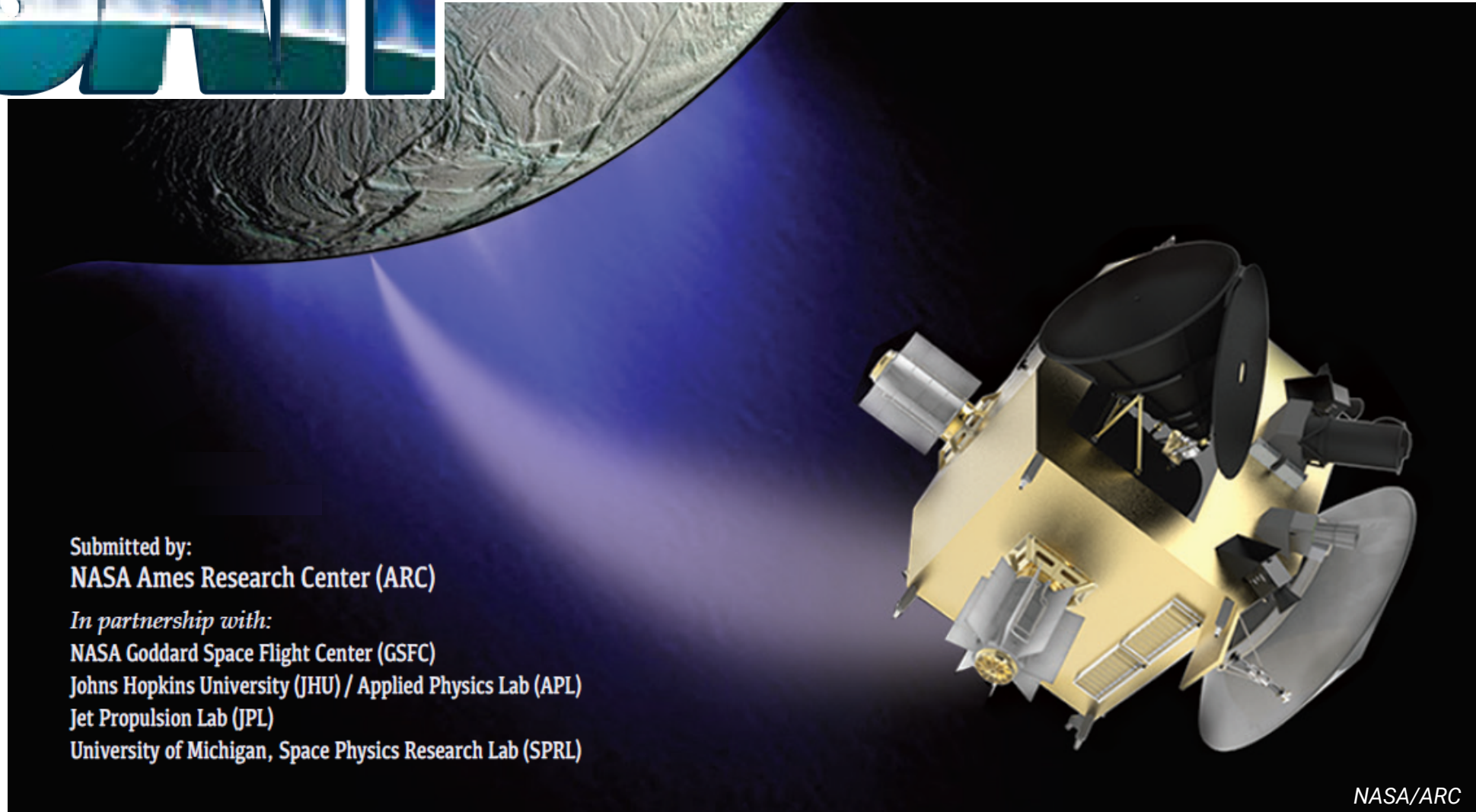


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8	L-Val	1
9	D-Ala	10
10	L-Ser	10
11	β-Ala	25
12	L-Ala	25
13	Gly	3

ELSAH

Mission Concept



Submitted by:
NASA Ames Research Center (ARC)

In partnership with:
NASA Goddard Space Flight Center (GSFC)
Johns Hopkins University (JHU) / Applied Physics Lab (APL)
Jet Propulsion Lab (JPL)
University of Michigan, Space Physics Research Lab (SPRL)

NASA/ARC

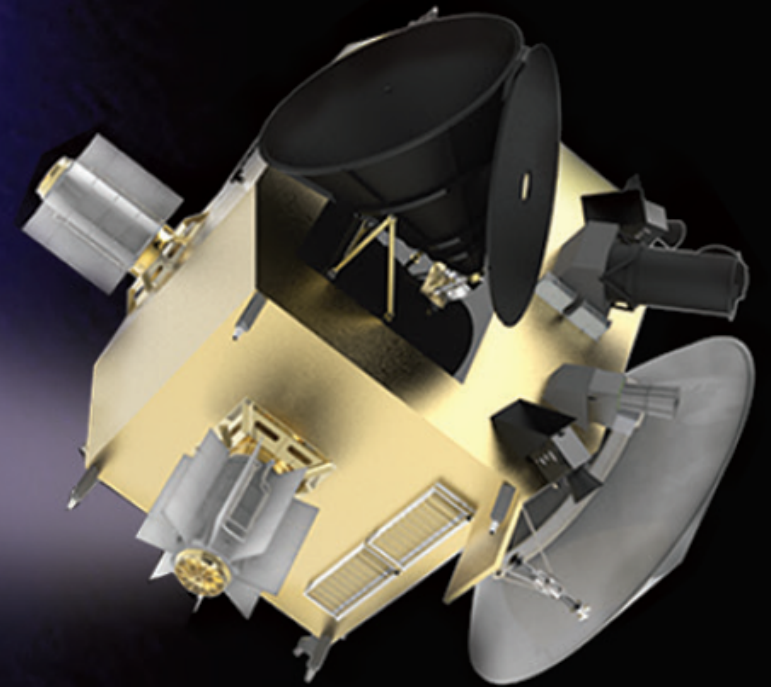
ELSAH

Mission Concept

Sample collection
from plume

Sample handling system
(SPLice)
including reagent storage

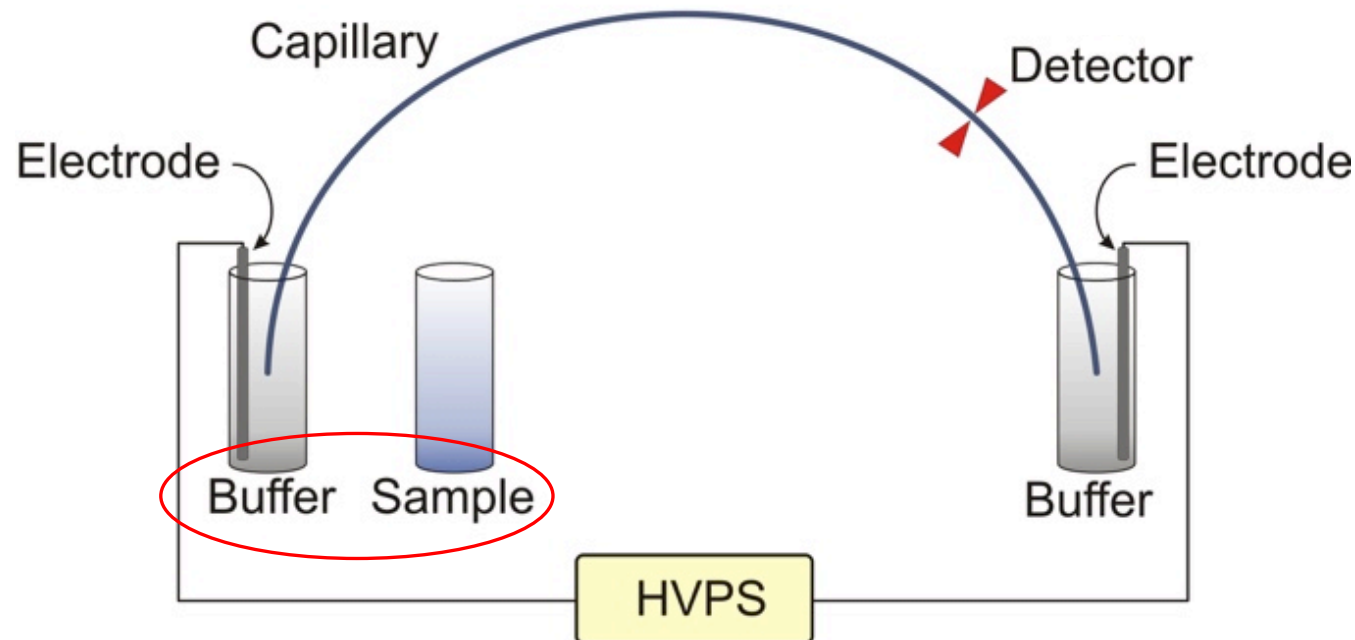
Capillary electrophoresis for
analysis of polar organics



Increasing the TRL of CE-LIF

Demonstrating stability of the hardware and chemicals under spaceflight environments

- Radiation
- Temperature

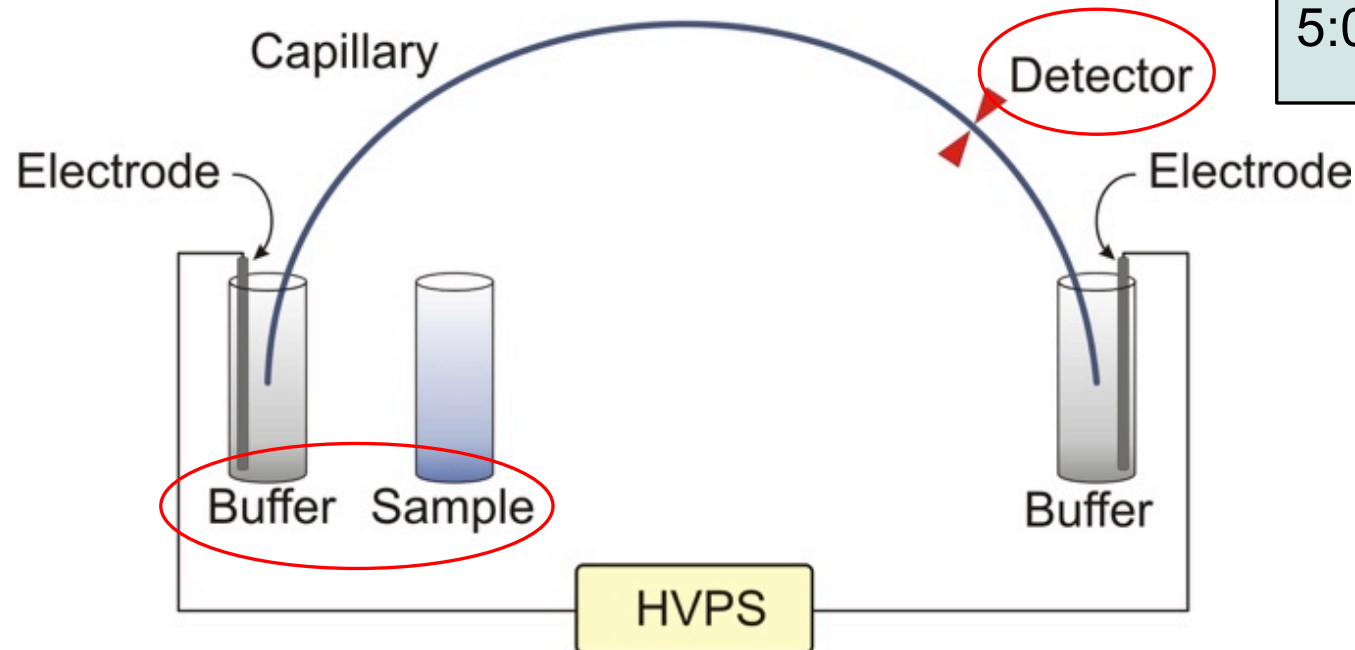


Increasing the TRL of CE-LIF

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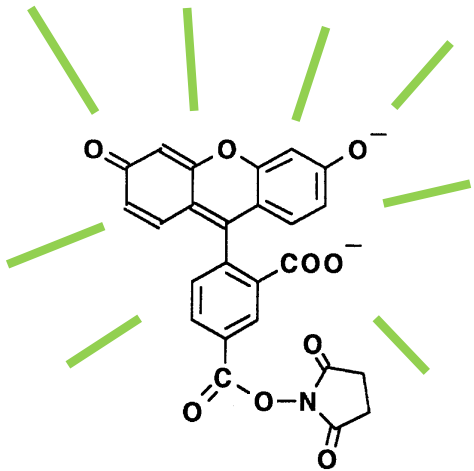
- Radiation
- Temperature

Nathan Oborny
Radiation Tolerant Hardware
Poster 139-146
Tonight!
5:00 – 7:00pm



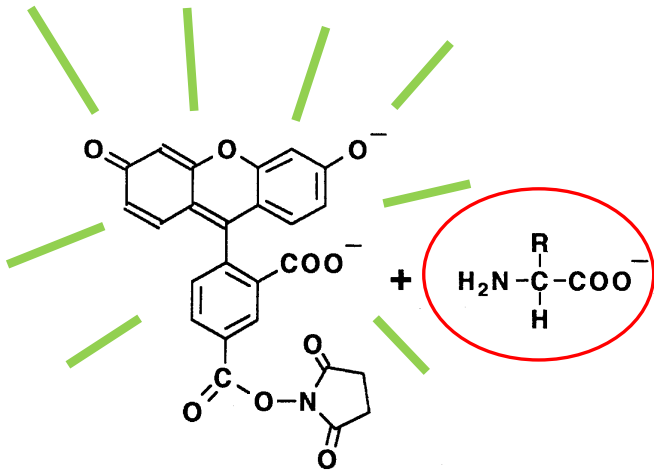
Chemical components of CE=LIF

Fluorescent Dye



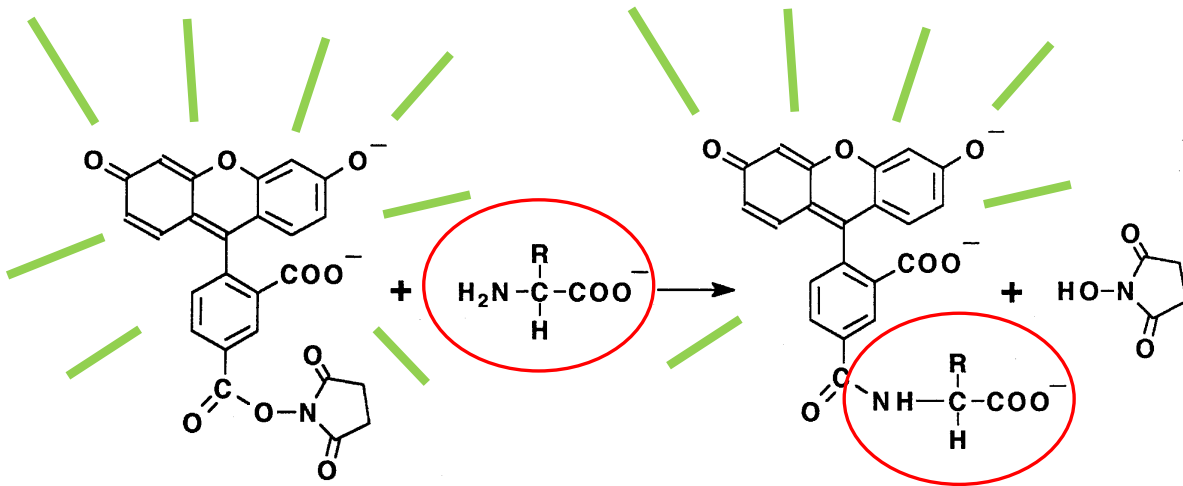
Chemical components of CE=LIF

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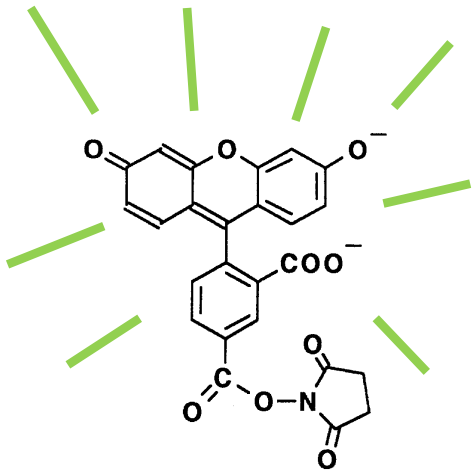
Chemical components of CE=LIF

Fluorescent Dye



Chemical components of CE=LIF

Fluorescent Dye



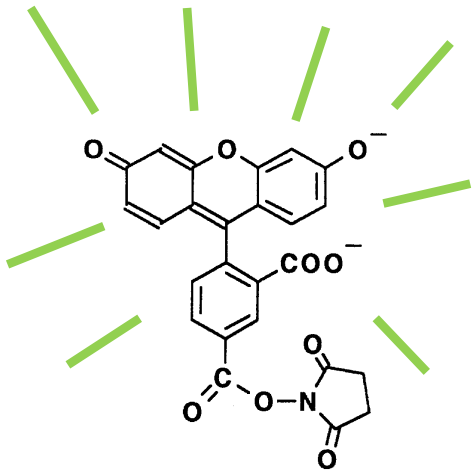
Background electrolyte

3 powdered reagents

Aqueous solution of
6% organic solvent
in water

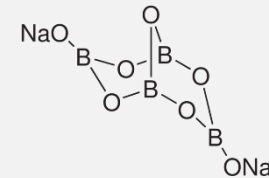
Chemical components of CE=LIF

Fluorescent Dye

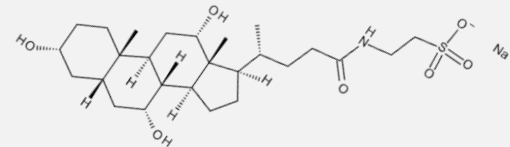


Background electrolyte

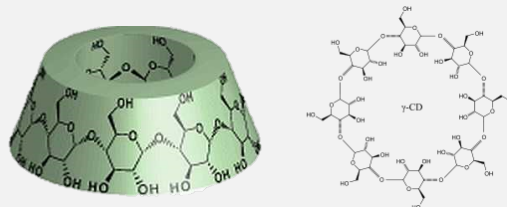
80 mM sodium tetraborate



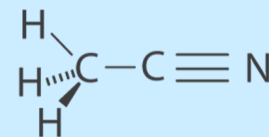
30 mM sodium taurocholate



30 mM γ -cyclodextrin



Water with
6% acetonitrile



Likely stored separately
to prevent precipitation
during a long transit

3 powdered reagents

Aqueous solution of
6% organic solvent
in water

Radiation tolerance

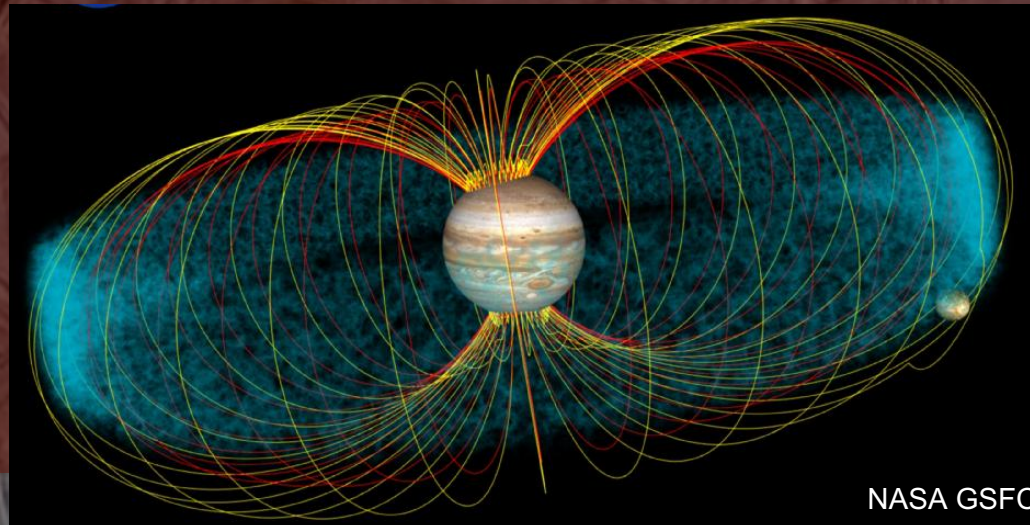
Europa represents the high end for radiation exposure during a mission

From the Europa Lander SDT Report:

Juno, and planned for the EMFM. Shielding by the lander vault would decrease the expected TID to 150 krad (Si). All electronics within the vault must be rated to 300 krad in order to maintain a radiation design factor of two ($RDF = 2$).

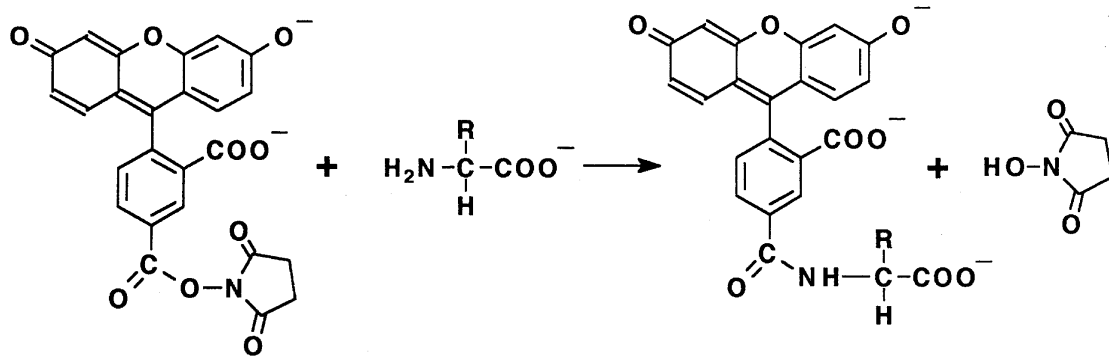
(Hand et al. 2017)

Pre-Decisional Information -- For Planning and Discussion Purposes Only

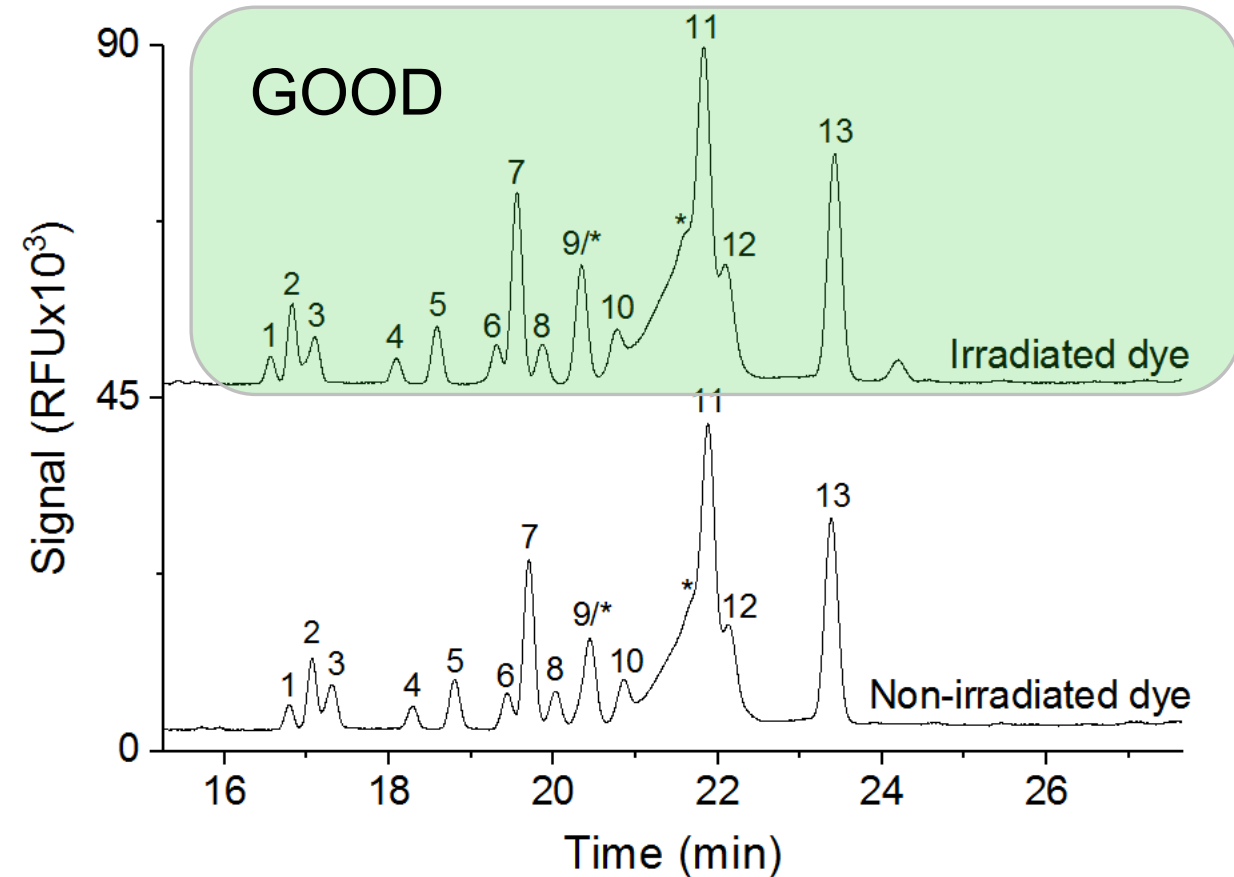


NASA GSFC

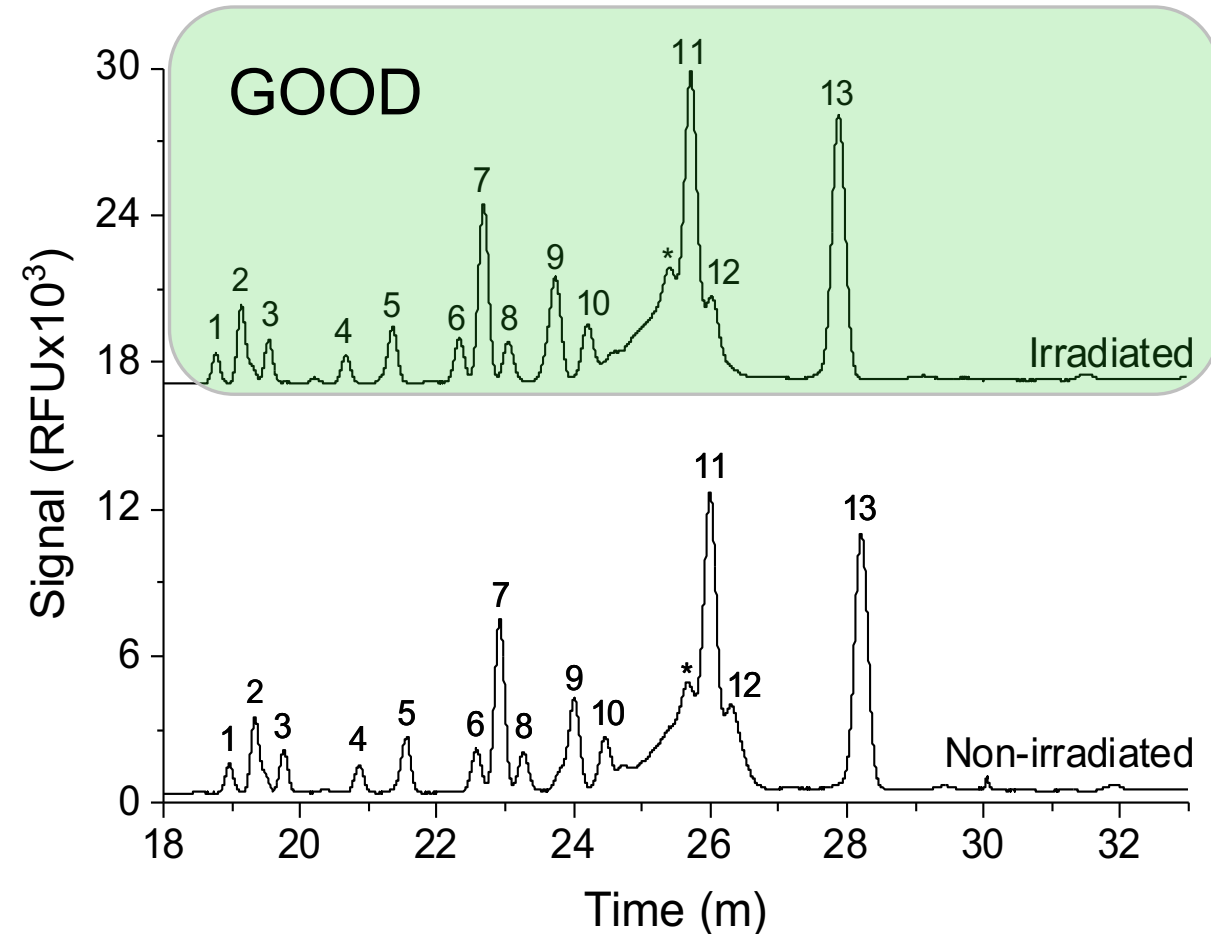
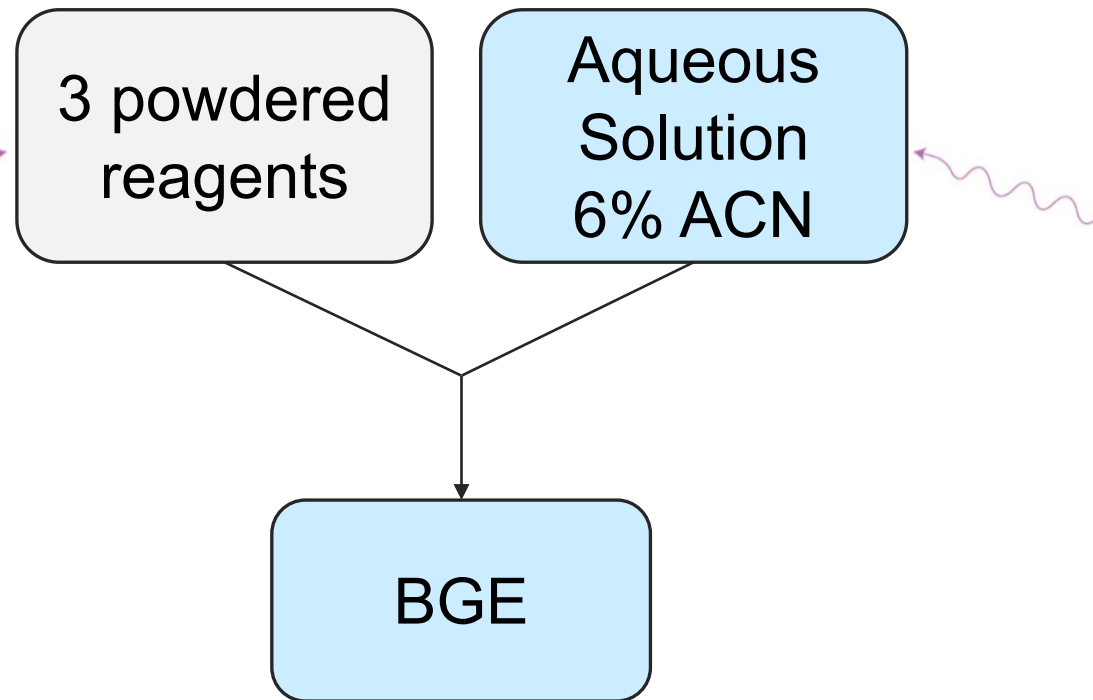
Fluorescent dye irradiation



- ✓ Retained **fluorophore**
- ✓ Retained succinimidyl ester **leaving group** needed to react with amino acids
- ✓ No interfering peaks due to radiolysis



Background Electrolyte Irradiation



Long-term storage at elevated temp

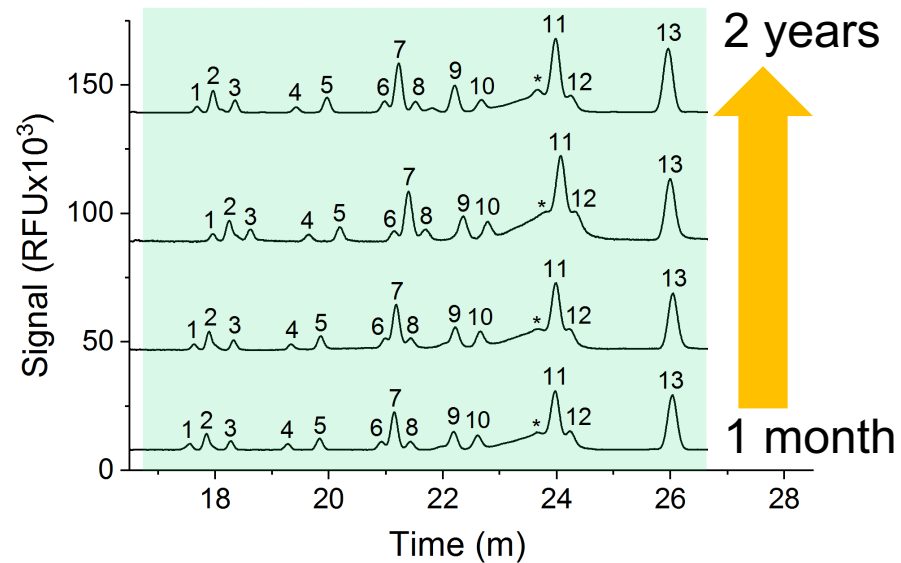
Fluorescent dye is sensitive to increased temperatures

- Recommended storage below -5 °C for one year

Long-term storage at elevated temp

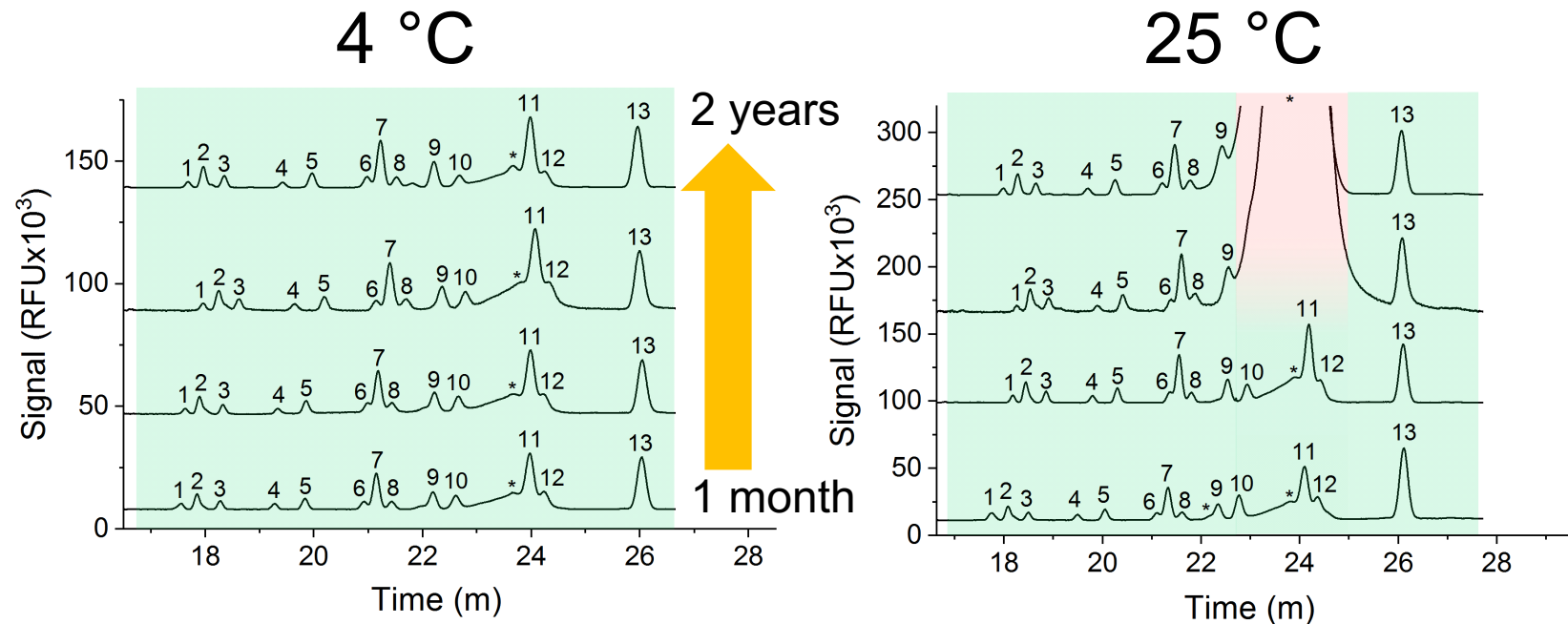
Tested dye after 1 month, 6 months, 1 year, and 2 years in storage

4 °C



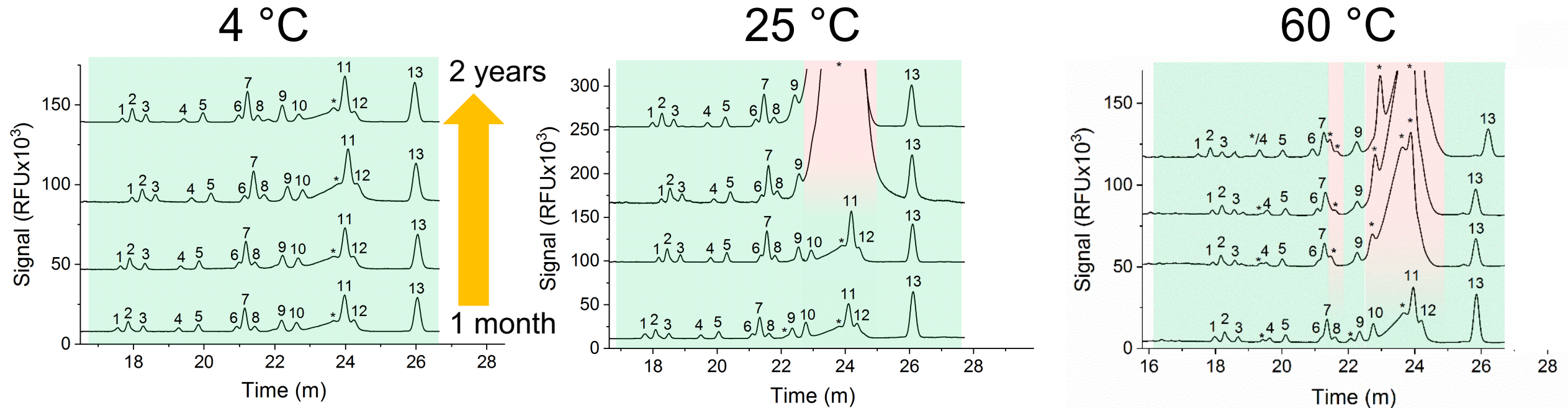
Long-term storage at elevated temp

Tested dye after 1 month, 6 months, 1 year, and 2 years in storage



Long-term storage at elevated temp

Tested dye after 1 month, 6 months, 1 year, and 2 years in storage



Conclusions

- CE-LIF is a separation technique that can simultaneously detect multiple astrobiologically relevant amino acids, with chiral resolution, and low limits of detection (≥ 1 nM)
- The chemicals needed to perform this CE-LIF analysis remain stable under radiation up to 300 krad
- Thermal control in the vault is needed to prevent the dye from experiencing more than 1 month above 60 °C
- This work represents a significant step forward towards validating the CE-LIF technique for spaceflight

Acknowledgments

- JPL NEXT Program funding the “OWLS – Ocean Worlds Surveyor” project
- NASA-PICASSO Program funding for the “Microfluidic Life Analyzer” project
- NASA Postdoctoral Program



Jet Propulsion Laboratory
California Institute of Technology



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